Mechanical, electrochemical and tribological properties of nanocrystalline surface of brass produced by sandblasting and annealing

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Abstract

Mechanical, electrochemical and tribological properties of nanocrystalline surfaces of a brass alloy (70–30) produced by sandblasting and annealing were investigated. The grain size of a nanocrystalline surface was determined by means of optical microscopy and transmission electron microscopy. The relationships between the grain size of a surface and its properties were investigated using nano-/micro-indentation, micro-scratch, electrochemical scratch and polarization techniques. It was demonstrated that the surface hardness and elastic behavior were improved as the grain size decreased, leading to markedly enhanced wear resistance. The efficiency of hardening by reduction of grain size became lower in the nanocrystalline region, compared to that in the microcrystalline region. The potentiodynamic polarization test indicated that the nanocrystalline surface had higher resistance to corrosion. Nano-indentation and micro-scratch test with in situ monitoring changes in contact electrical resistance demonstrated that the nanocrystallization was significantly beneficial to the mechanical behavior of the passive film. Mechanisms responsible for the beneficial effects of nanocrystallization on properties of brass and its passive films are briefly discussed.

Keywords: Nanocrystallization; Mechanical property; Electrochemical property; Passive film; Brass

1. Introduction

Reducing grain size is an important approach to improve mechanical properties of a polycrystalline material. In recent years, the mechanical behavior of nanocrystalline materials has been a subject of many studies [1,2]. The research of this topic is motivated by potential application of nanocrystalline materials thanks to their novel mechanical and physical properties.

Many experimental studies have shown that nanocrystallization can increase hardness of a material, resulting from increased grain boundaries that retard the motion of dislocations. In general, the hardness of a polycrystalline material increases with a decrease in grain size, obeying the well-known Hall–Petch (H–P) relationship [3,4].

\[ H = H_0 + kd^{-1/2} \]  

(1)

where \( H \) is the hardness, \( d \) is the grain diameter, and \( H_0 \) and \( k \) are material constants. For a regularly grained material, the value of \( k \) is positive. Although the dependence of hardness on the grain size has been widely applied in practice, it is not very clear whether the H–P relationship can be extended to the nanocrystalline region. Conflicting phenomena were reported by different researchers [5–7]. For instance, it was observed that a nanocrystalline NiAl obeyed the H–P relationship [12]; while the H–P relationship became unsuitable when the grain size was smaller than \( \sim 1 \) \( \mu \)m for polycrystalline Armco iron [8] and nickel [9]. Jang and Koch [10] reported that nanocrystallization could strengthen iron but the strengthening rate with respect to the grain size was low. It is also reported that nanocrystalline Ni–P is softer than coarse-grained polycrystalline Ni–P [11]. As a matter of fact, the grain boundary may block dislocations, thus strengthening a material. However, possible grain boundary sliding may render the material softer. Therefore, whether or not the crystallization can strengthen a material largely depends on the grain boundary structure and properties; the situation changes from case to case.

In addition to the mechanical behavior, other properties are also affected by nanocrystallization, e.g. corrosion behavior. For passive alloys, local break down of a
passive layer may lead to pitting corrosion [13–15]. The performance of a passive film formed on a nanocrystalline material could be very different from that of one on a conventional crystalline material. Recent studies on nanocrystalline 304 stainless steel have demonstrated that mechanical properties and the scratch resistance of the passive film on 304 stainless steel were markedly improved by nanocrystallization of the steel [16].

In many cases, failure of a work piece may initiate at surface, such as corrosion and wear. It is therefore effective and economical to modify the surface of a component for improved performance and prolonged service life. Surface nanocrystallization has attracted increasing interest. This paper reports our recent studies on surface nanocrystallization of brass (70–30) by sandblasting and annealing treatment. Such a nanocrystalline surface layer had a transition zone in which the grain size changed gradually from nano-scale to micro-scale, so that there was no problem with interface bonding. Effects of nanocrystallization on mechanical, electrochemical and tribological properties of the nanocrystalline surface were investigated. The influence of nanocrystallization on the passive film of brass was also studied.

2. Experimental procedure

Commercial brass (70–30) plates with dimensions of $35 \times 20 \times 3 \text{ mm}^3$ were used for the study. After ground using a 600 grit SiC paper, all samples were sand blasted under a blasting pressure 300 kPa for 10 min to produce nanocrystalline surface layers. The sand flow rate was 5 g/s. The mean roughness of the sandblasted surface was approximately 3 $\mu$m. The samples were then annealed at 150, 250, 350, 500 and 600 °C, respectively, for 1 h and cooled in air to obtain different grain sizes in the sandblasted surface layer. Surfaces of the samples were lightly polished using 0.05-$\mu$m alumina trioxide and etched with FeCl$_3$ + HCl. Some of the samples experienced passivation treatment in a 3.5% NaCl solution for 24 h. Such treatment may create a complex passive layer consisting of ZnO, CuCl and Cu$_2$O [15].

The crystalline size of a sample, after being etched in an alcoholic ferric chloride solution, was determined using optical microscopy. TEM (JEOL 2010) was employed to determine the size of grains in a nanocrystalline surface layer.

Microhardness of the samples was determined using a micro-indententer (from Fischer Technology, Inc.). Each hardness value is an average of 10 measurements. The ratio ($\eta$) of the elastic deformation energy to the total deformation energy, which reflects the elastic behavior of a material, was determined based on its loading–unloading curve [17].

The wear resistance of a surface was evaluated using a universal micro-tribometer (UMT) made by the Center for Tribology (CA, USA). During the test, a diamond tip scratched a surface under a constant load of 10 g at a velocity of 0.02 mm/s. The volume loss was determined.

A Gamry PC4/750 system was used to investigate the polarization behavior of the samples. The scan rate was 0.33 mV/s. A saturated calomel electrode was used as the reference electrode, and a piece of platinum was used as an auxiliary electrode.

A nano-mechanical probe with a pyramidal diamond indenter (Hysitron), was used to determine the hardness and $\eta$ values of passive films on the samples after the passivation treatment. The nano-indentation tests were performed in surface areas with their roughness (Ra) approximately equal to 0.02 $\mu$m. The force resolution of the instrument was 0.1 $\mu$N and the displacement resolution was 0.2 nm.

The resistance of a passive film to scratch was evaluated using the UMT. During the test, a diamond tip scratched a surface at a velocity of 0.02 mm/s under a normal load that was increased from 0 to a designed level. Failure of the passive film during scratch was determined by monitoring variations in the contact electrical resistance (CER) between the tip and the sample surface.

Corrosive wear of a sample was evaluated using an electrochemical scratch technique. During the test, a diamond tip scratched a sample surface immersed in a 3.5% NaCl solution under an applied potential and a constant load. Variations in current reflected the resistance of the surface to corrosive scratch. The tip velocity was 5 mm/s and the duration of scratching was 0.05 s.

3. Results and discussion

3.1. Grain size of the nanocrystalline surface

Surface microstructures and grain sizes of the sandblasted and annealed samples were examined under an optical microscope. Figs. 1(a)–(d) illustrate cross-sectional optical images of some of the samples. The thickness of the modified layer was approximately 25 $\mu$m. Since the grain size of the sample annealed at 150 °C could not be determined using the optical microscope, a transmission electron microscope (TEM) was employed to observe the nanocrystalline surface layer. Figs. 2(a) and (b) show bright- and dark-field images of a near-surface layer of the sample. One may see ultrafine grains that are equi-axed with their mean grain size approximately 20 nm. The corresponding diffraction pattern (Fig. 2a) indicates that the ultrafine grains were randomly oriented. After annealing at 250, 350, 500 and 600 °C, the grain size of the sandblasted surface layer increased as shown in Figs. 1(b) and (c). Average grain
sizes of surface layers of the samples were 0.5, 6, 30 and 80 \( \mu \text{m} \), respectively. For comparison, the average grain size of the as-received brass was 25 \( \mu \text{m} \). The grain sizes and corresponding annealing temperatures are summarized in Table 1.

The nanocrystallization by sandblasting is similar to those caused by severe plastic deformation [18,19]. The sandblasting provided repeated impacts on a surface at a high speed and generated high-density dislocations. The resultant dislocations could be re-arranged under stress to form dislocation networks, leading to the formation of nanocrystallites separated by diffuse grain boundaries. Annealing is necessary to diminish dislocations and sharpen the grain boundaries.

3.2. Microhardness and elastic behavior

Surface microhardnesses of the sandblasted and annealed samples were determined. Results of the test under a maximum load of 30 mN are given in Table 1. As demonstrated, the blasted sample annealed at 150 °C was the hardest, approximately 3 times as hard as the sample annealed at 600 °C. The highest hardness corresponded to the smallest grain size.

It can be estimated that Hv increased linearly with \( d^{-1/2} \) (\( d \) is the average grain diameter). However, there were two distinct positive slopes of the Hv \( \sim d^{-1/2} \) curve separated at \( d \approx 1.2 \mu \text{m} \), as shown in Fig. 3. Below this critical \( d \), the strengthening efficiency by increasing the density of grain boundary became smaller. In other words, the slope of the Hv \( \sim d^{-1/2} \) curve decreased in the nanocrystalline region. Such a decrease in the strengthening efficiency could result from increased probability of grain boundary sliding when the grain size was reduced to nano-scale. Nevertheless, the nanocrystalline surface was considerably harder than regular polycrystalline surface, although the strengthening effect became lower as the grain size was decreased to nano-scale.

As shown in Table 1, the nanocrystallization also resulted in improved elastic behavior or higher \( \eta \) value (Fig. 4). This happened because the elastic limit or the yield strength was increased when the dislocation motion was retarded by grain boundaries. As demonstrated, \( \eta \)

![Fig. 1. Microstructure of sandblasted brass (70–30) samples annealed at different temperatures. (a) Annealed at 150 °C; (b) annealed at 350 °C; (c) annealed at 500 °C; (d) as-received.](image-url)
value of the nanocrystalline surface with its grain size equal to 20 nm was the highest and approximately 2
times as high as that of one annealed at 600 °C whose
grain size was approximately 80 μm.

3.3. Scratch wear test

Micro-scratch tests were performed to evaluate the wear resistances of the samples using the UMT. Scratch
tacks on the samples are shown in Figs. 5(a)–(d). During the test, a diamond tip scratched a sample at its cross section from the inside to the blasted surface under a constant normal load. The width and depth of the scratch track on a specific sample reflected its wear resistance. As shown in Figs. 5(a)–(d), the narrowest and shallowest scratch track was observed on the sample annealed at 150 °C, while the widest and deepest scratch track was observed on the sample annealed at 600 °C. That is, with the increase in grain size from 20 nm to 80 μm, the scratch resistance decreased significantly.

For quantitative results, cross-sectional profiles of the scratch tracks were measured and the volume losses (V) per unit length (1 μm) of different samples in their surface region were determined. Volume losses of the samples are illustrated in Fig. 6, which shows that the scratch resistance of the sample annealed at 150 °C was the highest, corresponding to the smallest grain size. With an increase in the annealing temperature, the scratch resistance was lowered significantly. The difference in volume loss reached one order of magnitude large, when the grain size changed from 20 nm to 80 μm. The increase in the wear resistance by nanocrystallization is consistent with the associated improvement in the mechanical behavior of the material.

3.4. Electrochemical behavior

Corrosion behavior of the nanocrystalline brass surface was investigated. In a chloride medium, brass develops a passive film that may consist of CuCl, ZnO and Cu₂O [13,15,20]. The repassivation ability of an alloy and properties of its passive film are important to surface damage of the alloy when attacked by electrochemical reaction. In order to investigate the effect of nanocrystallization on electrochemical behavior of brass alloy, polarization behavior of different samples in a 3.5% NaCl solution was determined and obtained polarization curves are illustrated in Fig. 7. It was demonstrated that the sand blasting and annealing at 150 °C significantly improved the polarization behavior of the brass, not only raising the corrosion potential (E_{corr}), but also shifting both cathodic and anodic currents to lower values. When using the passive current density as a measure to evaluate the corrosion behavior of a material, one may see that the performance of brass was

<table>
<thead>
<tr>
<th>Annealing T (°C)</th>
<th>Grain size (nm)</th>
<th>Hv</th>
<th>η value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>20</td>
<td>342.1</td>
<td>31.4</td>
</tr>
<tr>
<td>250 (surface layer)</td>
<td>500</td>
<td>241.4</td>
<td>24.7</td>
</tr>
<tr>
<td>250 (sub-surface layer, approximately 15 μm from the surface)</td>
<td>1200</td>
<td>232.9</td>
<td>23.1</td>
</tr>
<tr>
<td>350</td>
<td>6000</td>
<td>177.7</td>
<td>20.6</td>
</tr>
<tr>
<td>As-received</td>
<td>25 000</td>
<td>154.2</td>
<td>17.9</td>
</tr>
<tr>
<td>500</td>
<td>30 000</td>
<td>127.5</td>
<td>17.3</td>
</tr>
<tr>
<td>600</td>
<td>80 000</td>
<td>115.1</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Maximum indentation load: 30 mN.
markedly improved as the grain size was decreased to nanoscale. The increase in the polarization behavior could be largely attributed to the formation of a better protective passive film on the nanocrystalline surface. In next sections, results of studies on the mechanical behavior and failure resistance of passive films on different samples are reported.

3.5. Failure of passive film during scratch

The passive film on brass is protective against corrosion [13,20]. In order to investigate possible benefits of nanocrystallization to passive film on brass, micro-scratch test was performed to evaluate the resistance of different sample surfaces to scratching. During the test, a diamond tip scratched a passivated surface under a linearly increasing load with in situ monitoring changes in CER. The critical normal load corresponding to the drop in the CER is a measure of the resistance of a passive film to scratch failure. Results of the scratch tests are presented in Figs. 8(a)–(e), respectively. Two curves in each figure represent the applied normal load and the CER, both of which are plotted against time. One may see that the passive film on the sample annealed at 150 °C failed when the load reached 8.3 g, while the failure loads for other samples were lower. As shown in Table 2, the larger the grain size of a surface, the lower was the scratch resistance of its passive film.

3.6. Mechanical properties of the passive film

In order to better understand the effect of nanocrystallization on passive film, mechanical properties of passive films on different samples were investigated using a nano-mechanical probe. Fig. 9 presents force–depth curves of different sample surfaces under two maximum loads, 50 and 100 μN. It should be indicated that the thickness of passive films is usually in the range of a few nanometers. After passivation, the passive films could be thicker. Therefore, under a light load, e.g. 50 μN, the indentation test may mainly reflect the mechanical behavior of the passive films, although the test results were, more or less, influenced by the substrate. Nevertheless, for comparable studies, the response of a passivated surface to nano-indentation under light loads may be considered as an approximate indicator of the mechanical behavior of its passive film. The maximum indentation depth and η values of the passive films were determined and results of the test are presented in Table 2. As shown, the surface of the blasted sample annealed at 150 °C had the smallest penetration depth and its η value was the highest. While the surface of the sample annealed at 600 °C was the softest with the lowest η value. The test demonstrated that the smaller the grain size of a surface, the better was the performance of its passive film.

The improved mechanical behavior due to nanocrystallization is attributed to several possible factors. The nanostructure with higher-density grain boundaries may promote diffusion and thus the formation of a more compacted passive film. In addition, the harder substrate may provide stronger support to the film. These could improve the performance of the passive film on a nanocrystalline substrate. However, further studies and especially the knowledge about the structure of the passive films are needed in order to draw a solid conclusion. The improved mechanical properties of a passive film were certainly beneficial to its resistance to scratch failure. It should be indicated that the enhanced scratch resistance could also benefit from possibly increased bonding strength of the interface between the passive film and its substrate. The high-density grain boundaries may help to increase the interfacial adherence, e.g. by possible development of oxide protrusions penetrating into grain boundaries, similar to oxide pegs of thick oxide scales on some ferrous alloys developed at grain boundaries at elevated temperatures [21].
3.7. Electrochemical scratch

It is expected that with the improved polarization behavior and the formation of a more protective passive film, the nanocrystallization could enhance the material against wear in corrosive environments. Electrochemical scratch test was performed to evaluate performances of different samples during scratching in a 3.5% NaCl solution. The test on a specific sample was carried out under an applied potential of 50 mV above $E_{\text{corr}}$ and a normal load of 20 g. The obtained current–time curves are shown in Fig. 10. When a passive alloy is scratched in a corrosive solution, the damage of passive film could enhance the material dissolution. When the scratch is...
finished, the current may quickly decrease caused by repassivation of the scratched surface. The increase in current ($\Delta i$, Fig. 10(a)) reflects the resistance of a surface to corrosive scratch. $\Delta i$ values of different samples are given in Table 3. The sample annealed at 150 °C, with nanocrystalline structure, showed the lowest increase in current. As the annealing temperature was raised, which resulted in an increase in the grain size, $\Delta i$ increased. As shown, $\Delta i$ of the sample annealed at 150 °C was approximately 20 times smaller than that of the one annealed at 600 °C. It was demonstrated that the nanocrystallization considerably improved the material resistance to corrosive scratch. The beneficial effect of nanocrystallization may also be seen from an approximate shaded area under the $i$–$t$ curve as shown in Fig. 10a, which is proportional to the total amount of

![Fig. 8. Variations in the electrical contact resistance of samples with respect to the scratch load. (a) Annealed at 150 °C; (b) annealed at 250 °C; (c) annealed at 350 °C; (d) annealed at 500 °C; (e) annealed at 600 °C.](image_url)
Table 3
Changes in current during electrochemical scratch

<table>
<thead>
<tr>
<th>Annealing T (°C)</th>
<th>150</th>
<th>250</th>
<th>350</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δi (A)</td>
<td>0.57×10^{-6}</td>
<td>0.64×10^{-5}</td>
<td>0.70×10^{-5}</td>
<td>0.90×10^{-5}</td>
<td>1.02×10^{-5}</td>
</tr>
</tbody>
</table>

Fig. 9. Surface load–depth curves of different samples obtained during nano-indentation. (a) Annealed at 150 °C; (b) annealed at 250 °C; (c) annealed at 350 °C; (d) annealed at 500 °C; (e) annealed at 600 °C.

dissolved material caused by electrochemical scratching [22]. As demonstrated, the sample annealed at 150 °C with nanocrystalline surface had significantly lower material loss, compared to the surfaces having larger grains. The superior resistance of the nanocrystalline surface to electrochemical scratching should result from its improved surface mechanical and electrochemical properties.

4. Conclusions

Research was conducted to investigate mechanical, electrochemical and tribological properties of nanocrystalline surfaces of brass produced by sand blasting and annealing. The mean grain size was 20 nm and the grain size increased as the annealing temperature was raised. It was demonstrated that a nanocrystalline surface
Fig. 10. \( i-t \) curves of samples scratched in a 3.5% NaCl solution under a potential of 50 mV. The samples were, respectively, annealed at (a) 150 °C; (b) 250 °C; (c) 500 °C; (d) 600 °C.

was significantly harder and more elastic than a regularly grained surface. However, the strengthening efficiency by increasing the density of grain boundaries decreased as the grain size was reduced to nano-scale. As a result of the improvement in mechanical behavior by nanocrystallization, the wear resistance of brass was enhanced.

The research demonstrates that the polarization behavior of nanocrystalline surface was superior to that of a regularly grained surface. Mechanical behavior and resistance to scratch failure of the passive film on brass were considerably improved by nanocrystallization. The improvements in mechanical and electrochemical properties by nanocrystallization effectively enhanced the resistance of brass surface to corrosive scratch or wear in a dilute NaCl solution.

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